

# Synthesis and Characterization of Methanesulfonate and Ethanesulfonate Intercalated Lithium Aluminum LDHs

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## Abstract

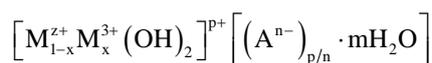
LDH-phases become increasingly interesting due to their broad ability to be able to incorporate many different cations and anions. The intercalation of methanesulfonate and ethanesulfonate into a Li-LDH as well as the behavior of the interlayer structure as a function of the temperature is presented. A hexagonal  $P6_3/m$   $[\text{LiAl}_2(\text{OH})_6][\text{Cl}\cdot 1.5\text{H}_2\text{O}]$  (Li-Al-Cl) precursor LDH was synthesized by hydrothermal treating of a LiCl solution with  $\gamma\text{-Al}(\text{OH})_3$ . This precursor was used to intercalate methanesulfonate ( $\text{CH}_3\text{O}_3\text{S}^-$ ) and ethanesulfonate ( $\text{C}_2\text{H}_5\text{O}_3\text{S}^-$ ) through anion exchange by stirring Li-Al-Cl in a solution of the respective organic Li-salt (90°C, 12 h). X-ray diffraction pattern showed an increase of the interlayer space  $c'$  ( $d_{001}$ ) of Li-Al-methanesulfonate (Li-Al-MS) with 1.2886 nm and Li-Al-ethanesulfonate (Li-Al-ES) with 1.3816 nm compared to the precursor with 0.7630 nm. Further investigations with Fourier-transform infrared spectroscopy and scanning electron microscopy confirmed a complete anion exchange of the organic molecules with the precursor  $\text{Cl}^-$ . Both synthesized LDH compounds  $[\text{LiAl}_2(\text{OH})_6]\text{CH}_3\text{SO}_3\cdot n\text{H}_2\text{O}$  ( $n = 2.24\text{-}3.72$  (Li-Al-MS) and  $[\text{LiAl}_2(\text{OH})_6]\text{C}_2\text{H}_5\text{SO}_3\cdot n\text{H}_2\text{O}$  ( $n = 1.5$ ) (Li-Al-ES) showed a monomolecular interlayer structure with additional interlayer water at room temperature. By increasing the temperature, the interlayer water was removed and the interlayer space  $c'$  of Li-Al-MS decreased to 0.87735 nm (at 55°C). Calculations showed that a slight displacement of the organic molecules is necessary to achieve this interlayer space. Different behavior of Li-Al-ES could be observed during thermal treatment. Two phases coexisted at 75°C - 85°C, one with a reduced  $c'$  (0.9015 nm, 75°C) and one with increased  $c'$  (1.5643 nm, 85°C) compared to the LDH compound at room temperature. The increase of  $c'$  is due to the formation of a bimolecular interlayer structure.

## Keywords

LDH, Lithium, Aliphatic Sulfonic Acid, X-Ray Powder Diffraction, High Temperature PXRD, Layered Double Hydroxides, Sulfonate

## 1. Introduction

Layered double hydroxides (LDHs) consist of alternate positively charged mixed metal hydroxide layers and negatively charged interlayer anions and can be normally described by the formula:



with  $z = 2$ ,  $M = \text{bi- and trivalent metallic elements}$ ,  $A = \text{organic or inorganic anions}$  and  $m = \text{amount of interlayer } \text{H}_2\text{O}$  depending on the relative humidity, hydration level and temperature [1] [2]. The ratio of  $M^{2+}$  to  $M^{3+}$  can be variable [3]. Unlike other LDHs, lithium-containing LDHs are based on the  $\text{Al}(\text{OH})_3$  structure with a solid cation ratio of 1:2 (Li:Al). The  $\text{Al}(\text{OH})_3$  structure is built up of double-layered sheets of hexagonally packed O atoms. Two-thirds of the octahedral holes are occupied by Al Atoms. During a LDH synthesis with  $\text{LiX}$  ( $X = \text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ , etc.), the remaining third will be occupied by Li Atoms which will lead to the 1:2 ratio [1] [4] [5] [6] [7].

The positive charged main layer must be compensated by a negative charge. This is achieved by the intercalation of anions in the interlayer. These can be both inorganic (e.g.  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ) and organic (e.g.  $\text{CH}_3\text{O}_3\text{S}^-$ ) anions [1] [8] [9] [10] [11]. The interlayer space depends on the type and size respectively chain length and the orientation of the intercalated anion [12]. In the present study, the successful synthesis of Li-Al-LDHs with intercalated methanesulfonate ( $\text{CH}_3\text{O}_3\text{S}^-$ ) and ethanesulfonate ( $\text{C}_2\text{H}_5\text{O}_3\text{S}^-$ ) anions as well as the possible interlayer structure as a function of the temperature is reported. These typical intercalation reactions of LDH-phases and their varying interlayer arrangements are of high interest of layered structures of LDH-type with a main layered metal of ion charge (+1), and the varying compositions and probable applications of these different intercalated LDH phases.

## 2. Experimental and Analytical Work

### 2.1. Reagents

The materials used within this work were  $\text{LiCl}$  (Roth, purity  $\geq 99\%$ ),  $\gamma\text{-Al}(\text{OH})_3$  (Merck, purity  $\geq 98\%$ ),  $\text{LiOH}$  (AppliChem, purity  $\geq 99\%$ ),  $\text{CH}_4\text{O}_3\text{S}$  (Lancaster, purity  $\geq 98\%$ ) and  $\text{C}_2\text{H}_5\text{O}_3\text{S}$  (Merck, purity  $\geq 98\%$ ). All chemicals tested by powder X-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) for purity and loss on ignition (LOI). As methanesulfonic acid and ethanesulfonic acid are in liquid state at room temperature, they were neutralized by  $\text{LiOH}$  and transformed into solid

lithium salts prior to the use in the investigations.

## 2.2. Methods

For PXRD investigations at room temperature, a PANalytical X'PERT<sup>3</sup> Powder diffractometer with a Pixcel detector and Cu radiation (45 kV/40 mA) was used. Approximately 1 g of the respective sample was prepared in a standard sample holder by back loading procedure and recorded from  $4^\circ - 70^\circ 2\theta$  with a step width of  $0.013^\circ 2\theta$  and the irradiation time of 20.41 s per step. High temperature PXRD between  $25^\circ\text{C}$  and  $400^\circ\text{C}$  were performed by a PANalytical X'PERT Pro MPD (Cu, 45 kV/40 mA) with an Anton-Paar high temperature chamber and a X'Celerator detector. The respective sample was prepared on a platinum band and recorded from  $2^\circ - 50^\circ 2\theta$  with a step width of  $0.0167^\circ 2\theta$  and an irradiation time of 19.69 s. To record the LOI and determine the type of the vaporized molecule, thermogravimetric analysis with parallel differential scanning calorimetry (TGA/DSC) and coupled mass spectrometer (MS) were performed using a NETZSCH STA449 F3 Jupiter and a NETZSCH QMS 403 D Aëolos. The samples were heated up from  $25^\circ\text{C}$  to  $1000^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  within an Argon atmosphere. The chemical composition and the 1:2 ratios between Li and Al of the main layer were proofed using a Horiba Ultima 2 inductively coupled plasma optical emission spectroscopy (ICP-OES). FT-IR spectra were recorded with a Bruker Tensor II spectrometer ( $400 - 4000 \text{ cm}^{-1}$ ) to verify the complete anion exchange and the intercalation of the organic molecules. Sample pictures were taken by a JOEL 640 scanning electron microscope (SEM). In addition, energy dispersive X-ray spectroscopy (EDX) was performed to detect a possible remainder of precursor  $\text{Cl}^-$ .

## 2.3. Synthesis

Methanesulfonic acid and ethanesulfonic acid were used in the reaction to the newly formed Li-salts by neutralizing the respective acid with LiOH until a pH of 7 - 7.5 was reached. The LDH  $[\text{LiAl}_2(\text{OH})_6][\text{Cl}\cdot 0.5\text{H}_2\text{O}]$  (Li-Al-Cl) was selected as the precursor due to the easy interchangeability of the  $\text{Cl}^-$  anion [13] and synthesized by a variation of the hydrothermal method [13] [14]. A good crystalline precursor was achieved by adding 1 g of  $\gamma\text{-Al}(\text{OH})_3$  to 15 ml of a LiCl solution with a few drops of 0.5 mole LiOH (pH 8 - 8.5). The educt ratio of Al:Li was 1:5 [15] [16]. The suspension was heated to  $100^\circ\text{C}$  for 10 hours in an autoclave. After completion of the synthesis the product was filtered, washed with 50 ml deionized  $\text{H}_2\text{O}$ , dried to a relative humidity (RH) of 35% and analyzed for purity and amount of crystal water. To exchange  $\text{Cl}^-$  for methanesulfonate or ethanesulfonate, 1 g of the precursor was added to 25 ml deionized  $\text{H}_2\text{O}$  and so much of the respective Li-salt was added that a ratio of  $\text{Cl}^-:\text{X}^-$  ( $\text{X}^-$  = organic anion) of 1:2 was obtained. The suspensions were heated up to  $90^\circ\text{C}$  for 12 h under constant stirring. After completion of the synthesis, the products were filtered, washed with 50 ml deionized  $\text{H}_2\text{O}$  and dried to 35% RH. The entire syn-

thesis processes were performed in a glove box with N<sub>2</sub> atmosphere to avoid carbonization.

### 3. Results and Discussion

#### 3.1. TGA/DSC-MS and ICP-OES Analysis

Exactly 10 mg of the respective LDH were dissolved in 0.5 ml suprapure 65% HNO<sub>3</sub>, diluted with 10 ml deionized H<sub>2</sub>O and measured with ICP-OES. The results showed the expected Li/Al ratio of 1:2 and no leftover of Cl<sup>-</sup> from the precursor. The amount of interlayer water and the amount of the absorbed organic molecule was determined by TGA/DTA-MS with approximately 10 mg of the respective LDH. The mass losses can be divided in three steps for both sulfonate containing LDHs. The interlayer water is removed between 25 °C and 200 °C with a total of 2.24 mol H<sub>2</sub>O for Li-Al-methanesulfonate (Li-Al-MS) and 3.72 mol H<sub>2</sub>O for Li-Al-ethanesulfonate (Li-Al-ES). The decomposition of the main layer starts at approx. 250 °C and continues to 295 °C. By removing the OH groups of the main layer at these elevated temperatures, the crystal structure is destroyed and the LDH compounds become X-ray amorphous. The last large mass loss lies between 400 °C and 500 °C and is caused by the breakdown of the organic compounds. Due to the mass spectroscopy, it was possible to differentiate between H<sub>2</sub>O and the organic molecules, which could be measured as fragments in the form of e.g. CH<sup>+</sup> or SO<sup>2+</sup>. The chemical composition of both LDH compounds were therefore calculated (Table 1).

#### 3.2. FT-IR Spectroscopy

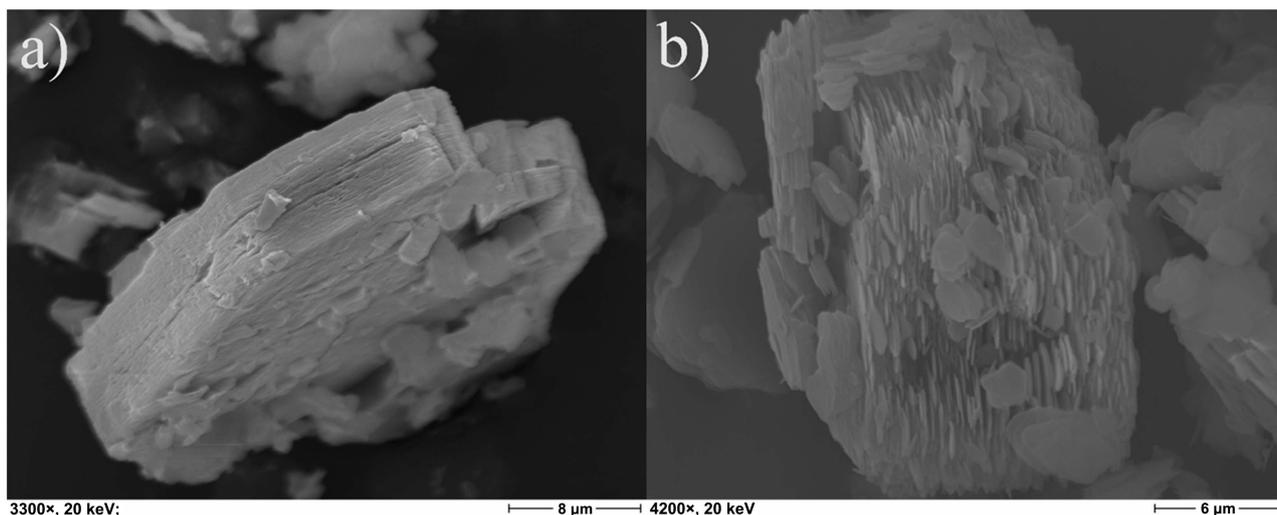
Li-Al-MS and Li-Al-ES were investigated by FT-IR to proof the intercalation of the organic molecules and the noncarbonization of the relevant synthesis products. Both sulfonate LDHs showed the typical SO<sub>3</sub><sup>2-</sup> ( $\nu$  1055 cm<sup>-1</sup>,  $\nu_{as}$  1202 cm<sup>-1</sup>,  $\nu_3$  1242 cm<sup>-1</sup>,  $\nu_{as}$  1292 cm<sup>-1</sup>), CH<sub>3</sub> ( $\delta_s$  1373 cm<sup>-1</sup>), H<sub>2</sub>O ( $\nu_2$  1627 cm<sup>-1</sup>), OH ( $\nu$  3400 - 3600 cm<sup>-1</sup>) and Al-OH ( $\delta$  752 cm<sup>-1</sup>,  $\delta$  940 cm<sup>-1</sup>) absorptions. Li-Al-ethanesulfonate showed also the CH<sub>2</sub> ( $\delta_s$  1417 cm<sup>-1</sup>,  $\nu_{as}$  2941 cm<sup>-1</sup>) absorptions of the methylene group [6] [17] [18] [19] [20]. No CO<sub>2</sub>/CO<sub>3</sub><sup>2-</sup> absorptions and therefore no carbonization of the compounds could be detected [6] [21].

#### 3.3. SEM (EDX) Analysis

The investigated samples were free of Cl<sup>-</sup> from the initial chemicals which proofed the complete anion exchange between the precursor and the sulfonate anions. Both LDHs formed flat hexagonal crystals with a clearly visible layered structure in crystallographic *c*-direction (Figure 1). The crystals of Li-Al-MS had an average size of 2 - 20 μm in crystallographic *a*-direction and 2 μm - 10 μm in crystallographic *c*-direction. In comparison, the crystals of Li-Al-ES were mostly smaller in the *a*-direction (1 - 10 μm) and showed strongly rounded crystal edges. These small crystals formed hexagonal clusters with layer thicknesses of up to 30 μm in *c*-direction.

**Table 1.** Calculated and measured compositions (mass %) of Li-Al-MS and Li-Al-ES (35% RH).

	$n_c$	Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	C <sub>n</sub> H <sub>2n+1</sub> SO <sub>3</sub> H	H <sub>2</sub> O	*interlayer	total
calculated	1	5.01	34.17	32.21	28.61		100.00
measured		5.07	34.07	31.24	28.56	(13.50)	98.94
calculated	3	4.41	30.07	32.48	33.04		100.00
measured		4.44	30.17	31.18	33.13	(19.78)	98.91

**Figure 1.** SEM pictures of (a) Li-Al-MS, (b) Li-Al-ES.

### 3.4. PXRD Analysis at 25°C

The distance between two layers within the LDH structure can be described by the layer distance  $c'$  ( $d_{001}$ ) and depends on the type, size and inclination angle of the intercalated anion. This inclination angle  $\alpha$  can be calculated by using the average increase of  $c'$  depending on the chain length ( $\Delta c'$ ). Ethanesulfonate molecule is larger and therefore (requires more space in the interlayer, which leads to an increase in the interlayer distance  $c'$ : **Table 2, Figure 2**).

With the calculated  $\Delta c' = 0.0928$  and the given formula  $\sin \alpha = \Delta c' / 0.127$ , the inclination angle of the intercalated molecules is  $\alpha = 46.95^\circ$  (35% RH) [9].

A Li-Al-LDH layer with intercalated sulfonate anions is normally composed of the positively charged main layer with 0.20 nm between the OH groups and 0.29 nm between the OH and the  $\text{SO}_3^{2-}$  group (**Figure 3**). The terminal methyl group of the organic anions occupies 0.30 nm and the H<sub>2</sub>O molecules 0.31 nm of the interlayer space. The occupied space by the remaining part of organic anion can be calculated with the formula:  $0.127 \text{ nm} \cdot (n_c - 1) \cdot \sin \alpha$  with  $n_c$  = number of carbon atoms [9]. Based on these data the interlayer space for both LDH compounds could be calculated (**Table 3**).

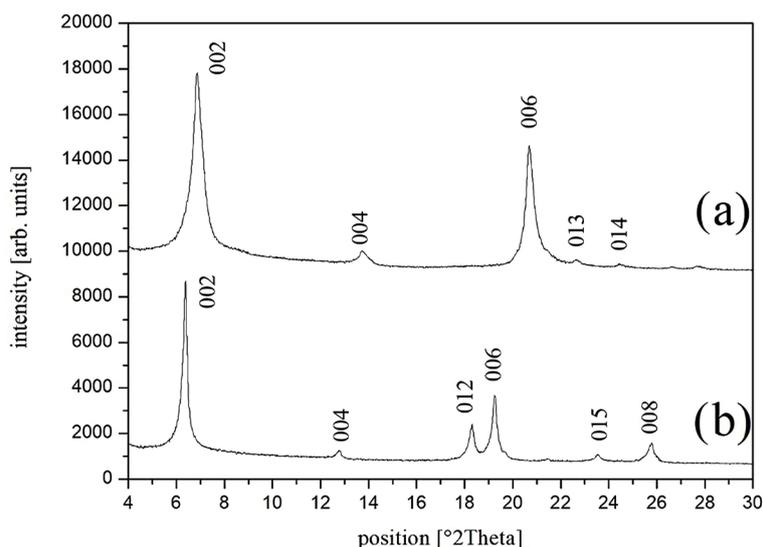
With only one layer of H<sub>2</sub>O molecules, the differences between the measured and calculated interlayer spaces are too high. By adding mathematically another half layer of H<sub>2</sub>O molecules within the calculation (0.47 nm instead of 0.31 nm),

**Table 2.** Lattice parameters and amount of interlayer water of Li-Al-Ms and Li-Al-ES.

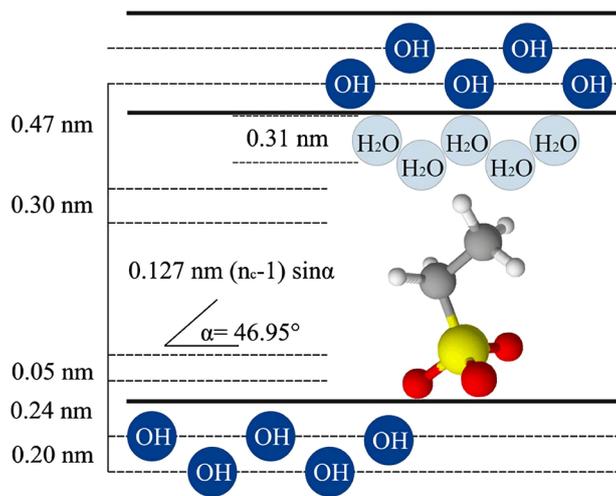
$n_c$	$a_0$ [nm]	$b_0$ [nm]	$c_0$ [nm]	$c'$ [nm]	$\beta$ [°]	H <sub>2</sub> O [mol]	space group
1	0.5109(6)		2.5772(7)	1.2886(3)		2.24	P6 <sub>3</sub> /m
2	0.5108(8)	0.5165(4)	2.7628(6)	1.3816(3)	92.01(7)	3.72	P2 <sub>1</sub> /c

**Table 3.** Calculated and measured interlayer space  $c'$  of Li-Al-MS and Li-Al-ES with 1 and 1.5 layer of interlayer H<sub>2</sub>O and an inclination angle of 46.95°.

$n_c$	1 layer of H <sub>2</sub> O molecules			1.5 layer of H <sub>2</sub> O		
	$c'_c$ [nm]	$c'_m$ [nm]	diff. [nm]	$c'_c$ [nm]	$c'_m$ [nm]	diff. [nm]
1	1.100	1.2886	0.1886	1.2600	1.2886	0.0286
2	1.1928	1.3816	0.1888	1.3528	1.3816	0.0288



**Figure 2.** XRD pattern of (a) Li-Al-ES, (b) Li-Al-MS with a shift of Li-Al-ES towards smaller  $2\theta$  due to the interlayer anion ethanesulfonate.



**Figure 3.** Example for the structure of a Li-Al-ES with an ethanesulfonate anion and 1.5 layers of H<sub>2</sub>O molecules (modified according to [9]).

the difference could be calculated and adjusted. It can therefore be assumed, that the H<sub>2</sub>O molecules within the interlayer are offset by the half length in *c*-direction to each other (Figure 3).

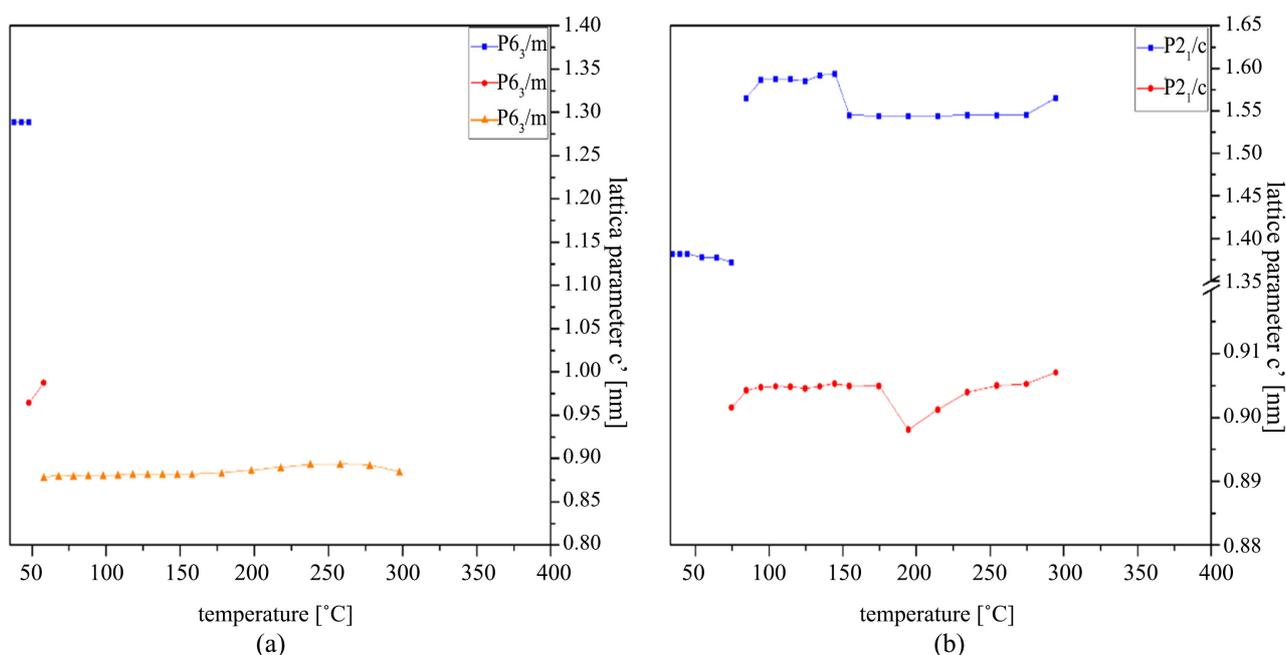
While Li-Al-MS crystallized in the hexagonal space group P6<sub>3</sub>/m, the space group of Li-Al-ES could be determined as monoclinic P2<sub>1</sub>/c. The lattice parameters were determined by Pawley fit based on a 2H Li-Al unit cell [15].

### 3.5. PXRD Analysis at Higher Temperatures

The behavior of the LDH phases as a function of temperature was investigated by heating the phases up to 400 °C. Pure Si was added as standard to the samples to compensate the platinum band expansion and zero shifts.

Li-Al-MS showed a decrease of the lattice parameter *c'* starting at 45 °C - 55 °C from the original 1.2286 nm to 0.9873 nm followed by a second decrease at 55 °C - 65 °C to 0.8773 nm where the interlayer space remained nearly constant until the decomposition of the main layer at 295 °C with *c'* = 0.8831 nm (Figure 4, Table 4). The space group P6<sub>3</sub>/m did not change at higher temperatures. Without interlayer H<sub>2</sub>O at temperatures above 200 °C the calculated interlayer space of Li-Al-MS is 0.79 nm. The difference of 0.0931 nm between the calculated and the measured *c'* (295 °C) can be explained by a slightly shift of the sulfonate molecules to each other at higher temperatures (Figure 5) [19] [22]. Both phases become X-Ray amorphous at about 300 °C due to the beginning destruction of main layer.

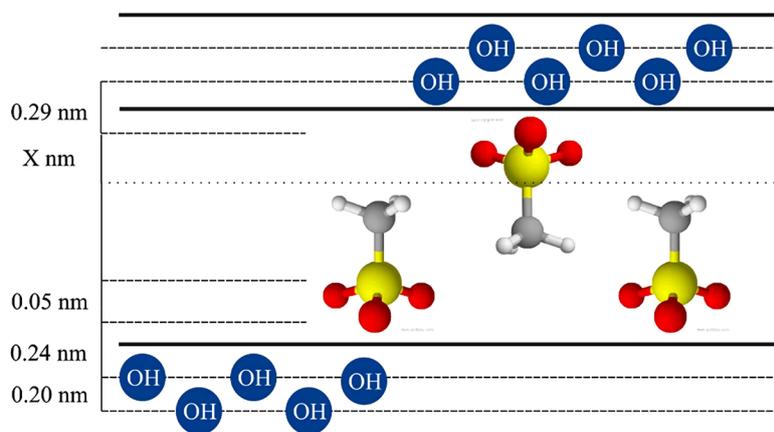
With a splitting in two different phases at 75 °C - 85 °C, Li-Al-ES did not show the same behavior. The interlayer spaces *c'* of the two phases are 0.9042 nm and 1.5643 nm at 85 °C. Assuming that the sulfonate anions can behave the same way



**Figure 4.** Shifts of lattice parameters *c'* depending on the temperature of (a) Li-Al-MS and (b) Li-Al-ES.

**Table 4.** Lattice distances  $c'$  of Li-Al-MS and Li-Al-ES depending on the temperature.

temp [°C]	lattice distance $c'$ [nm]				
	Li-Al-MS			Li-Al-ES	
	P6 <sub>3</sub> /m	P6 <sub>3</sub> /m	P6 <sub>3</sub> /m	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
25	1.2886			1.3814	
26	1.2884			1.3815	
35	1.2884			1.3815	
45	1.2886	0.9643		1.3811	
55		0.9873	0.8773	1.3775	
65			0.8786	1.3774	
75			0.8788	1.3716	0.9015
85			0.8791	1.5643	0.9042
95			0.8791	1.5866	0.9047
105			0.8799	1.5867	0.9048
115			0.8809	1.5868	0.9048
125			0.8807	1.5847	0.9045
135			0.8807	1.5916	0.9049
145			0.8806	1.5936	0.9052
155			0.8806	1.5443	0.9049
175			0.8821	1.5435	0.9049
195			0.8853	1.5435	0.8981
215			0.8887	1.5437	0.9012
235			0.8923	1.5447	0.9039
255			0.8923	1.5445	0.9050
275			0.8908	1.5448	0.9052
295			0.8831	1.5648	0.9070

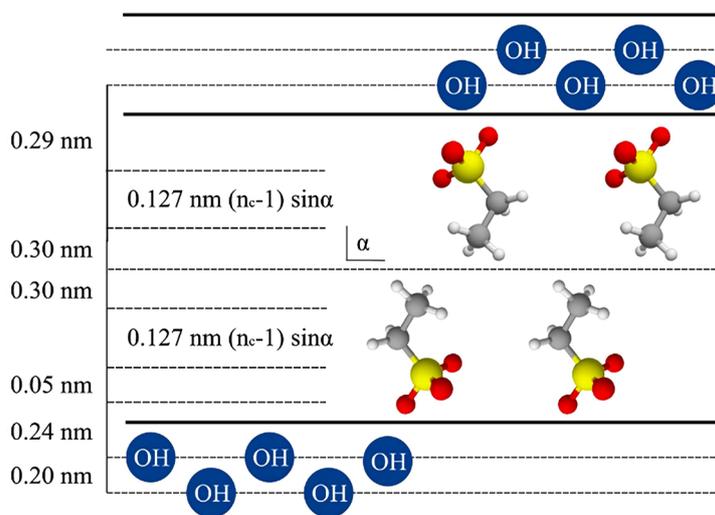
**Figure 5.** Interlayer structure of Li-Al-MS with a displacement of the methanesulfonate molecules for  $x$  nm in  $c$ -direction.

like aliphatic and aromatic monocarboxylic acids it is possible to form a “double” interlayer structure by placing two sulfonate anions above each other with an inclination angle of  $90^\circ$  (Figure 6). A doubled interlayer structure with  $\alpha = 90^\circ$  and without interlayer  $\text{H}_2\text{O}$  (due to the high temperature) has a calculated interlayer space of 1.5840 nm which fits extremely good with the measured  $c'$  of the “higher spaced” phase (Table 4). Using only one layer of sulfonate anions in the interlayer structure and  $\alpha = 90$  for the calculation results in  $c'_{\text{calc}} = 0.9170$  nm, which also fits precisely with the measured interlayer spaces (Table 4).

Li-Al-ethanesulfonate hydrate with the lower interlayer phase is therefore a coexisting single layer version of the phase with an “increased interlayer space”. No change of the monoclinic space group  $P2_1/c$  during the heating process could be found.

### 3.6. Infrared Spectroscopy

Li-Al-LDHs with intercalated methanesulfonate (Figure 7) and ethanesulfonate (Figure 8) were also investigated by IR-spectroscopy and their spectra and interpretations (Table 5 and Table 6) are reported.



**Figure 6.** Interlayer structure of Li-Al-ES with a double layer of the ethanesulfonate molecules and an inclination angle of  $90^\circ$ .

**Table 5.** IR spectroscopic data of  $[\text{LiAl}_2(\text{OH})_6]\text{X}$   $\{\text{X} = \text{CH}_3\text{SO}_3\}_n \cdot n\text{H}_2\text{O}$ .

vibration $\text{cm}^{-1}$		type of vibration
3600 - 3400	$\nu(\text{OH})$	(OH)—valence vibration—main layer
	$\nu_1, \nu_3(\text{H}_2\text{O})$	(H-O-H)—valence vibration—interlayer water
2943	$\nu_{\text{as}}(\text{CH}_2)$	asym. (C-H)—valence vibration of $\text{CH}_2$ -group
1630	$\nu_2(\text{H}_2\text{O})$	(H-O-H)—valence vibration—inter layer water
1417	$\delta_s(\text{CH}_2)$	sym. (C-H)—deformation vibration of $\text{CH}_2$ -group
1373	$\delta_s(\text{CH}_3)$	sym. (C-H)—deformation vibration of $\text{CH}_3$ -group
1292	$\nu_{\text{as}}(\text{SO}_3^{2-})$	asym. ( $\text{SO}_3^{2-}$ )—valence vibration

Continued

1242	$\nu_3(\text{SO}_3^{2-})$	$(\text{SO}_3^{2-})$ —valence vibration
1202	$\nu_{as}(\text{SO}_3^{2-})$	asym. $(\text{SO}_3^{2-})$ —valence vibration
1055	$\nu(\text{SO}_3^{2-})$	$(\text{SO}_3^{2-})$ —valence vibration
1001	$\delta_{\text{in-pl.}}(\text{CH})$	(C-H)—deformation vibration in plane
934	$\delta \text{Al-OH}$	(Al-OH)—deformation vibration
759	$\delta \text{Al-OH}$	(Al-OH)—deformation vibration
535	$(\text{AlO}_6)$	(AlIV-O)—vibration
460	LiO	(Li-O)—vibration

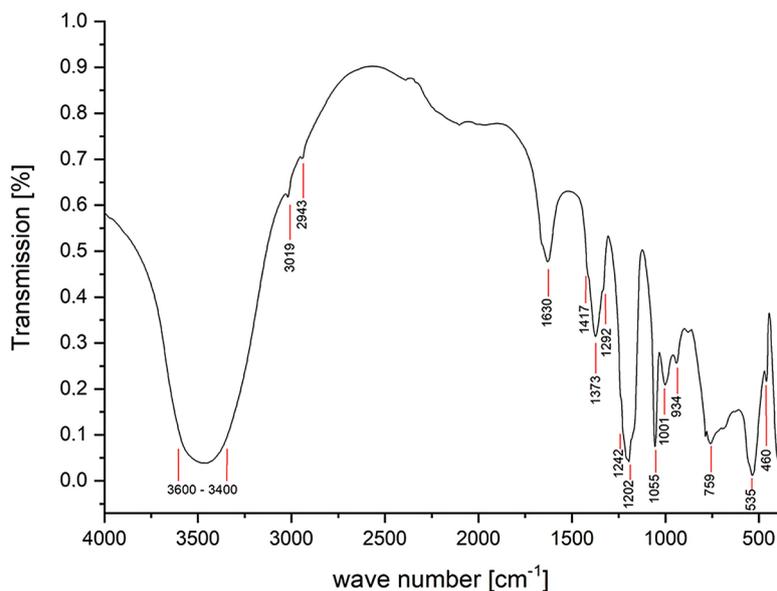


Figure 7. IR spectroscopy of  $[\text{LiAl}_2(\text{OH})_6]\text{X} \{ \text{X} = \text{CH}_3\text{SO}_3 \} \cdot n\text{H}_2\text{O}$ .

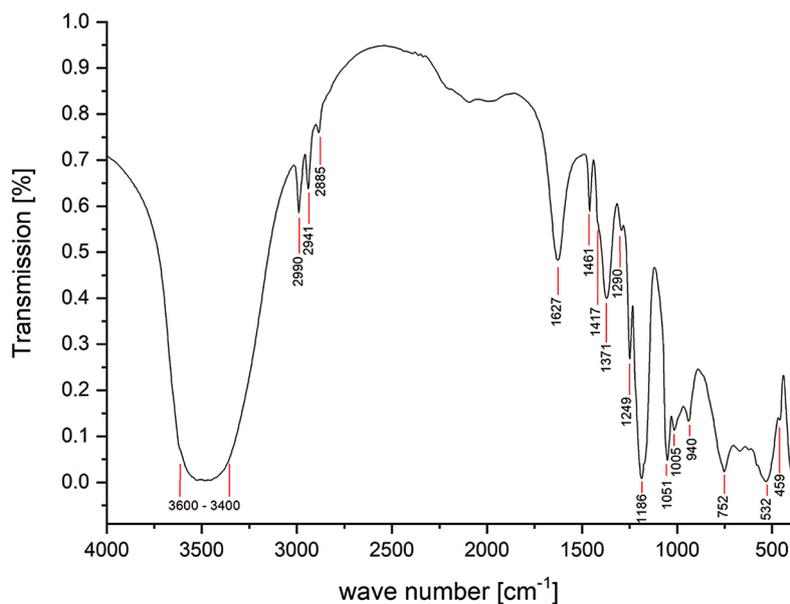


Figure 8. IR spectroscopy of  $[\text{LiAl}_2(\text{OH})_6]\text{X} \{ \text{X} = \text{C}_2\text{H}_5\text{SO}_3 \} \cdot n\text{H}_2\text{O}$ .

**Table 6.** IR spectroscopic data of  $[\text{LiAl}_2(\text{OH})_6]\text{X}$   $\{\text{X} = \text{C}_2\text{H}_5\text{SO}_3\} \cdot n\text{H}_2\text{O}$ .

vibration	$\text{cm}^{-1}$	Type vibration
3600 - 3400	$\nu(\text{OH})$	(OH)—valence vibration—main layer
	$\nu_1, \nu_3(\text{H}_2\text{O})$	(H-O-H)—valence vibration—interlayer water
2990	$\nu_{as}(\text{CH}_3)$	asym. (C-H)—valence vibration of $\text{CH}_3$ -group
2941	$\nu_{as}(\text{CH}_2)$	asym. (C-H)—valence vibration of $\text{CH}_2$ -group
2885	$\nu_s(\text{CH}_2)$	sym. (C-H)—valence vibration of $\text{CH}_2$ -group
1627	$\nu_2(\text{H}_2\text{O})$	(H-O-H)—valence vibration—interlayer water
1461	$\delta_{as}(\text{CH}_3)$	asym. (C-H)—deformation vibration of $\text{CH}_3$ -group
1417	$\delta_s(\text{CH}_2)$	sym. (C-H)—deformation vibration of $\text{CH}_2$ -group
1371	$\delta_s(\text{CH}_3)$	sym. (C-H)—deformation vibration of $\text{CH}_3$ -group
1290	$\nu_{as}(\text{SO}_3^{2-})$	asym. ( $\text{SO}_3^{2-}$ )—valence vibration
1249	$\nu_3(\text{SO}_3^{2-})$	( $\text{SO}_3^{2-}$ )—valence vibration
1186	$\nu(\text{SO}_2)$	( $\text{SO}_3^{2-}$ )—valence vibration
1051	$\nu(\text{SO}_3^{2-})$	( $\text{SO}_3^{2-}$ )—valence vibration
1005	$\delta_{\text{in-pl.}}(\text{CH})$	(C-H)—deformation vibration within plane
940	$\delta\text{Al-OH}$	(Al-OH)—deformation vibration
752	$\delta\text{Al-OH}$	(Al-OH)—deformation vibration
532	( $\text{AlO}_6$ )	(Al-O)—vibration
459	LiO	(Li-O)—vibration

The different vibrations of  $[\text{LiAl}_2(\text{OH})_6]\text{X}$   $\{\text{X} = \text{CH}_3\text{SO}_3\} \cdot n\text{H}_2\text{O}$  were interpreted in **Table 5**.

The different vibrations of  $[\text{LiAl}_2(\text{OH})_6]\text{X}$   $\{\text{X} = \text{C}_2\text{H}_5\text{SO}_3\} \cdot n\text{H}_2\text{O}$  were interpreted in **Table 6**.

## 4. Conclusions

The synthesis of crystalline and pure Li-Al-LDHs with intercalated methanesulfonate and ethanesulfonate by the anion exchange method using a Li-Al-Cl precursor is easily possible.

The following compositions were determined:

1) Li-Al-MS (Methylsulfonate)



2) Li-Al-ES (Ethylsulfonate)



Calculations showed that the organic molecules were intercalated not in a flat arrangement, but with an inclination angle of  $\alpha = 46.95^\circ$  at  $25^\circ\text{C}$ . By increasing the temperature, the inclination angle changed to  $90^\circ$ . Li-Al-ES also showed a complete change of a part of the interlayer structure by stacking two organic molecules on top of each other (bimolecular) at higher temperatures. The other

part remained in an unstacked single layer structure (monomolecular). The coexistence of both phases could be explained by a new formed superstructure arrangement. While Li-Al-MS remains in a monomolecular structure, the displacement of the organic molecules may indicate an incomplete formation of a bimolecular structure. By changing the environmental temperature, the inter-layer structure and distance can be controlled.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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